

Carrier concentrations in $\text{Bi}_{2-\delta}\text{La}_z\text{CuO}_{6+\delta}$ single crystals and their relation to Hall coefficient and thermopower

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We measured the thermopower S and the Hall coefficients R_H of $\text{Bi}_{2-\delta}\text{La}_z\text{CuO}_{6+\delta}$ (BSLCO) single crystals in a wide doping range, in an effort to identify the actual hole concentrations per Cu, p , in this system. It is found that the “universal” relation between the room-temperature thermopower and T_c does not hold in the BSLCO system. Instead, comparison of the temperature-dependent R_H data with other cuprate systems is used as a tool to identify the actual p value. To justify this approach, we compare normalized $R_H(T)$ data of BSLCO, $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ (LSCO), $\text{YBa}_2\text{Cu}_3\text{O}_y$, and $\text{Tl}_2\text{Ba}_2\text{CuO}_{6+\delta}$, and demonstrate that the $R_H(T)$ data of the LSCO system can be used as a template for the estimation of p . The resulting phase diagram of p vs T_c suggests that T_c is anomalously suppressed in the underdoped samples, becoming zero at around $p \simeq 0.10$, while the optimum T_c is achieved at $p \simeq 0.16$ as expected.

PACS numbers: 74.25.Dw, 74.25.Fy, 74.62.-c, 74.72.Hs

Determination of the actual carrier concentration in the high- T_c cuprates is in general a difficult task. The La-214 system [$\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ (LSCO) or $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ (LBCO)] is almost the only system where the carrier concentration is nearly unambiguously known; in this system, the hole concentrations per Cu, p , is identical to the x value, as long as the oxygen is stoichiometric. In the $\text{YBa}_2\text{Cu}_3\text{O}_y$ (YBCO) system, the hole concentration in the CuO_2 planes is ambiguous because of the existence of the imperfect CuO chains which absorb part of the doped holes. In other systems like $\text{Bi}_{2-\delta}\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ (Bi-2212), $\text{Bi}_{2-\delta}\text{Sr}_2\text{CuO}_{6+\delta}$ (Bi-2201), or $\text{Tl}_2\text{Ba}_2\text{CuO}_{6+\delta}$ (Tl-2201), the determination of the hole concentration is also ambiguous because Bi and Tl ions have mixed valencies [1].

In ordinary metals or semiconductors, the Hall coefficient R_H is often used for the determination of the carrier concentration. However, R_H of the cuprates has not been considered to be a useful tool to determine p , because R_H shows a rather strong temperature dependence. Moreover, it has been reported for LSCO that the magnitude of R_H is several times smaller than that expected from the chemically-determined carrier concentration [2]. On the other hand, it has been proposed [3] that the magnitude of the thermopower at room temperature (290 K), denoted as $S(290\text{K})$, can be used for the determination of p , based on the observation that the plot of T_c/T_c^{max} vs $S(290\text{K})$ is almost “universal” among many cuprates (T_c^{max} is the optimum T_c of each system), although the data of the LSCO system do not follow the “universal” relation [4]. If one assumes another “universal” relation [5] between p and T_c/T_c^{max} , so-called the “bell shape”, the measurement of $S(290\text{K})$ yields an estimation of p as long as the two “universal” relations hold.

The above mentioned relation between p and $S(290\text{K})$ has not been tested in $\text{Bi}_{2-\delta}\text{La}_z\text{CuO}_{6+\delta}$ (BSLCO, or

La-doped Bi2201), in which the carrier concentration can be changed over a wide range [6]. An increase in the La concentration z in this system leads to a smaller density of holes in the CuO_2 planes, and the optimum T_c is achieved with $z \simeq 0.4$. In this paper, we report our systematic measurements of $S(290\text{K})$ and $R_H(T)$ for a series of BSLCO single crystals, for which z is varied from 0.2 to 1.0. It is found that the optimally-doped BSLCO crystal show notably smaller $S(290\text{K})$ value than that expected from the “universal” relation. This is a strong indication that the “universal” relation does not hold in the BSLCO system and thus one should not use this relation to determine p . We therefore tried to use the temperature-dependent R_H for the determination of p . We show that, using $R_H(T)$ of the LSCO system as a template, the $R_H(T)$ data can give reasonable estimate of p . With the p values thus obtained, we construct the relation between p and $S(290\text{K})$, which is actually quite different from the “universal” relation. The final phase diagram of T_c vs p for the BSLCO system suggests that T_c is anomalously suppressed in the underdoped samples, becoming zero at around $p \simeq 0.10$, while the optimum T_c is achieved at $p \simeq 0.16$.

The single crystals of $\text{Bi}_{2-\delta}\text{La}_z\text{CuO}_{6+\delta}$ are grown using a floating-zone (FZ) technique [6]. Here we report crystals with z from 0.23 to 1.02. The crystal with $z=0.39$ is optimally-doped; the optimum T_c is 36 K, which is very high for BSLCO [6] and indicates that the crystals reported here are among the best crystals available to date. The actual La concentration in the crystals are determined by employing both the inductively-coupled plasma analysis and the electron-probe microanalysis. For the transport measurements, the crystals are cut into dimensions of typically $2 \times 1 \times 0.05 \text{ mm}^3$. Since the absolute magnitude of the Hall coefficient is important for this work, the thickness of the samples is accurately

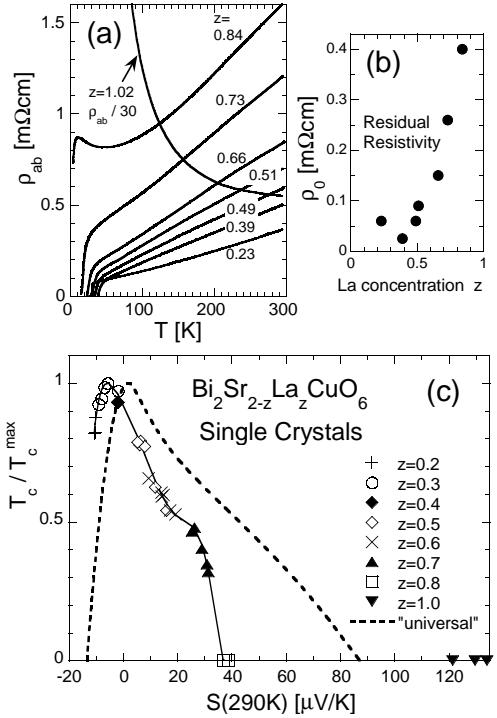


FIG. 1. (a) $\rho_{ab}(T)$ data of the BSLCO crystals for selected z values. (b) z dependence of ρ_0 obtained from Fig. 1(a). (c) T_c/T_c^{\max} vs $S(290\text{K})$ of the BSLCO crystals, plotted together with the “universal” relation [3] reproduced as a dashed line. The z values shown in this panel are nominal values. The solid line is a guide to the eyes.

determined by measuring their weight with 0.1- μg resolution, and the uncertainty in the absolute magnitude of R_H is estimated to be less than $\pm 8\%$. All the crystals are annealed in flowing oxygen at 650°C for 48 hours to guarantee uniform oxygen distribution in the samples.

We define T_c in this paper by the onset of the Meissner effect measured by dc magnetic susceptibility. We have confirmed that the Meissner-onset T_c agrees very well with the zero-resistance T_c for our crystals [6]. The Hall coefficient R_H is measured together with the in-plane resistivity ρ_{ab} by using a standard six probe technique. The current contacts are carefully painted to cover two opposing side faces of the platelet-shaped crystals to ensure a uniform current flow. The voltage contacts are painted on the two remaining side faces of the crystals (not on the top or bottom faces), which is important for the accurate Hall effect measurement. The Hall coefficients are measured by sweeping the magnetic field to both plus and minus polarities, while the temperature is stabilized by a combination of the calibrated Cernox sensor and a capacitance sensor [6]. The thermopower is measured with a standard steady-state technique with a reversible temperature gradient of $\sim 1\text{ K}$, and the thermopower of the gold wires are corrected for.

Figure 1(a) shows the $\rho_{ab}(T)$ data of the BSLCO crystals for selected z values from 0.23 - 1.02, which show systematic evolution with changing carrier concentration. One may notice that the residual resistivity ρ_0 of these samples [7] becomes systematically larger with increasing La doping, although ρ_0 is very small ($\sim 20\ \mu\Omega\text{cm}$) at optimum doping; the z dependence of ρ_0 is plotted in Fig. 1(b). Figure 1(c) shows the plot of T_c/T_c^{\max} vs $S(290\text{K})$ of our BSLCO crystals ($T_c^{\max} = 36\text{ K}$), together with the “universal” relation [3] reproduced as a dashed line. It is clear that the two curves do not agree at all. This is either because the universal relation between p and $S(290\text{K})$ does not hold in the BSLCO system or because the T_c values are somehow reduced from the ideal value (and thus does not correctly reflect the hole concentrations). To determine which is actually the case, we pay attention to the peaks in Fig. 1(c), which corresponds to the optimum doping; if we can find an evidence from another experiment that the optimum T_c of BSLCO is indeed realized at $p \simeq 0.16$, it is a clear indication that the universal relation of T_c/T_c^{\max} vs $S(290\text{K})$ is disobeyed in BSLCO. Note that the $S(290\text{K})$ value of the optimally-doped BSLCO sample ($\sim -6\ \mu\text{V/K}$) corresponds to $p \simeq 0.22$ in the “universal” relation [3].

We now demonstrate that the magnitude of the Hall coefficient can be used as a guide to estimate p . It has been pointed out [4] that the fictitious carrier density calculated from the room-temperature value of R_H does not vary much among different cuprates at the same hole concentration. Therefore, if R_H is normalized by the unit volume V and the number of Cu atoms in the unit, N , the resulting R_H/NV is expected to show similar values for different cuprates at optimum doping ($p \simeq 0.16$). Note that $R_H e/NV$ (e is the electronic charge) gives the inverse of the fictitious hole density per Cu. Figure 2(a) shows the plot of $R_H e/NV$ vs T for various cuprates, LSCO, YBCO, Tl-2201, and BSLCO, at optimum doping. The data for Tl-2201 is taken from Ref. [8], and all other data are measured by ourselves paying particular attention to the accuracy in the absolute magnitude. The LSCO sample is a high-purity polycrystal [9], and the YBCO sample is a high-quality single crystal grown by a flux method using Y_2O_3 crucible [10]. In the R_H data of LSCO and YBCO, the uncertainty in the absolute magnitude is less than $\pm 8\%$. It is clear in Fig. 2(a) that the normalized R_H of all the optimally-doped cuprates shown here agree reasonably well in the temperature range 150 - 300 K, where the data fall in a rather narrow band of $\sim 20\%$. This observation is remarkable and has not been emphasized before in the literature. For the purpose of this paper, Fig. 2(a) strongly suggests that it is reasonable to assert p to be actually around 0.16 in our optimally-doped BSLCO crystal.

Figure 2(b) shows the comparison of $R_H e/NV$ vs T for LSCO and YBCO at three representative dopings: optimum doping, 1/8 doping, and the superconductor-

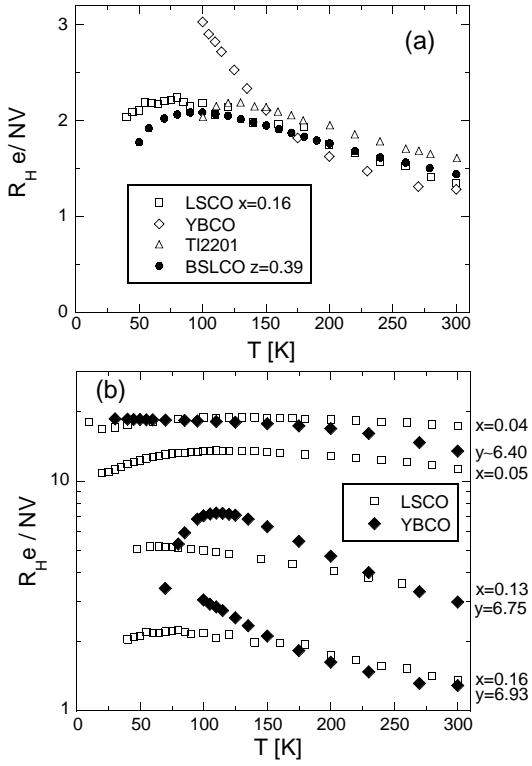


FIG. 2. (a) Plots of $R_H e/NV$ vs T for various optimally-doped cuprates, LSCO ($x=0.16$), YBCO ($y=6.93$), Ti-2201, and BSLCO ($z=0.39$). The data for Ti-2201 is taken from Ref. [8]. Note that all the data lie in a rather narrow band of $\sim 20\%$ in the temperature range 150 - 300 K, implying that $R_H e/NV$ can be a good measure of the hole concentration. (b) Comparison of $R_H e/NV$ of LSCO and YBCO at three representative dopings: optimum doping, $1/8$ doping, and the superconductor-insulator boundary ($p \simeq 0.05$).

insulator (S-I) boundary ($p \simeq 0.05$). For YBCO, it has been reported [11] that the 60-K phase ($y \simeq 6.7$) corresponds roughly to $p \simeq 1/8$ and the S-I boundary ($y \simeq 6.4$) lies at $p \simeq 0.05$. Therefore, because of the special physical meanings attached to these hole concentrations, the three dopings shown in Fig. 2(b) give good reference points where the p values are well-defined. One can see in Fig. 2(b) that the $R_H e/NV$ data of the two systems agree reasonably well at the three dopings at temperatures above ~ 200 K. This observation gives further support to the idea that $R_H e/NV$ can be used as a guide to estimate p ; the comparison shown in Fig. 2(b) suggests that the data of LSCO system, for which p is nearly unambiguous, can be used as a template to compare the data of other systems.

Based on the above observation, we try to estimate p of our BSLCO crystals by comparing the $R_H e/NV$ data with that of LSCO. Figure 3 shows the data of the two systems for selected concentrations. From Fig. 3, one can infer that the La concentration, z , of 0.73 corresponds to $p \simeq 0.12$, $z=0.84$ to $p \simeq 0.10$, and $z=1.0$ to $p \simeq 0.03$.

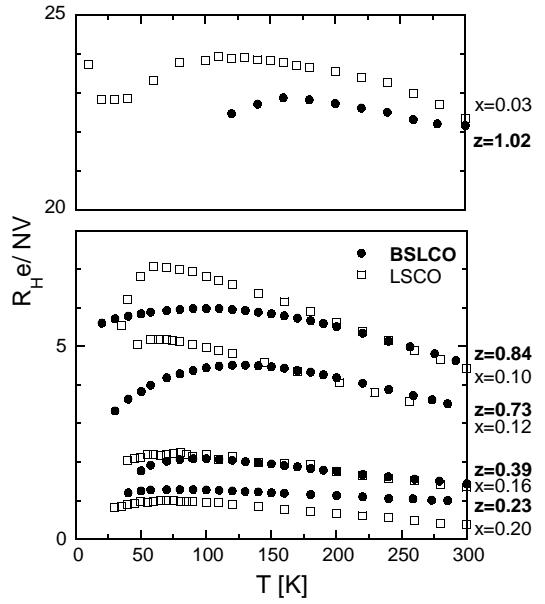


FIG. 3. Comparison of $R_H(T)e/NV$ of LSCO and BSLCO at various hole concentrations.

Based on this observation, we determine the p values for various z as follows: $p = 0.18, 0.16, 0.15, 0.14, 0.13, 0.12, 0.10$, and 0.03 , for $z = 0.23, 0.39, 0.49, 0.51, 0.66, 0.73, 0.84$, and 1.02 , respectively [12]. Note that these determination are not precise and the expected accuracy would be $\pm 10\%$ at best [13]. This result implies that the superconductivity of our BSLCO is about to disappear at $z=0.84$ *not* because the hole concentration is reduced to $p \sim 0.05$. Remember that there is a tendency that ρ_0 becomes systematically larger with increasing La doping, as shown in Fig. 1(b). This suggests that one possible reason for the disappearance of superconductivity at $z \simeq 0.9$ (which corresponds to $p = 0.09 - 0.10$) is the increased disorder in the heavily-La-doped crystals. In other words, in our BSLCO samples the superconductivity is more significantly suppressed in more underdoped samples because of the larger amount of disorder probed by ρ_0 . The microscopic origin of this disorder triggered by heavy La doping is yet to be elucidated; it is difficult to imagine that the random potential produced by the replacement of Sr with La itself is responsible to produce ρ_0 of as large as $400 \mu\Omega\text{cm}$.

Figure 4 shows the plot of $S(290\text{K})$ vs p for our BSLCO crystals (where p is determined as above), together with the “universal” relation that is reported to be valid for most of the cuprates except for LSCO [4]. Clearly, the BSLCO system does not follow the “universal” trend. The reason for this deviation is not clear, but it is intriguing to note that both BSLCO and LSCO are peculiar systems in which the optimum T_c is much lower than the “intrinsic” T_c (about 80 K) expected for single-layer cuprates. It has been discussed [14] that these two sys-

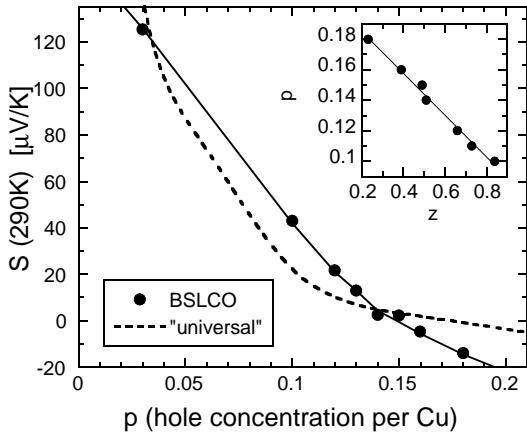


FIG. 4. $S(290K)$ vs p plot for the BSLCO crystals together with the “universal” relation [3]. The solid line is a guide to the eyes. Inset shows a plot of estimated p vs z , together with a straight line fit.

tems might share the common trend to stabilize charged stripes, which is known to suppress superconductivity [15].

Using the p values inferred for our BSLCO samples, we can estimate the fictitious T_c^0 values for each La concentration by assuming the ordinary “bell shape” [5] for T_c^0/T_c^{max} vs p ; this T_c^0 is the ideal value that would be expected for a given p if there were no cause for the reduction of T_c . Since ρ_0 of the $z=0.39$ sample is small [Fig. 1(b)], we assume that our optimum T_c is not significantly affected by disorder and thus we take $T_c^{max} = 36$ K for the calculation of T_c^0 . Figure 5 shows the plot of actual T_c vs p of the BSLCO system, together with the fictitious T_c^0 vs p . It is clear in Fig. 5 that $T_c(p)$ of the BSLCO system shows a faster drop in both the underdoped and overdoped sides of the phase diagram, which is probably caused by disorder as inferred from the increase in ρ_0 when z moves away from the optimum doping [Fig. 1(b)].

In summary, we estimate the hole concentration per Cu, p , of a series of BSLCO crystals by using the normalized Hall coefficient R_{He}/NV and its comparison with other cuprates. It is demonstrated that at optimum doping $R_H(T)e/NV$ of various cuprates (LSCO, YBCO, Tl-2201, and BSLCO) agree reasonably well in the temperature range 150 - 300 K, where the data fall in a rather narrow band of $\sim 20\%$. This implies that R_{He}/NV can be used as a guide to estimate p . It is found that in the BSLCO system the room-temperature thermopower $S(290K)$ as a function of p does not follow the “universal” trend. The phase diagram of T_c vs p for our BSLCO crystals suggests that T_c is anomalously suppressed in the underdoped samples, where the residual resistivity is found to increase systematically with increasing La doping.

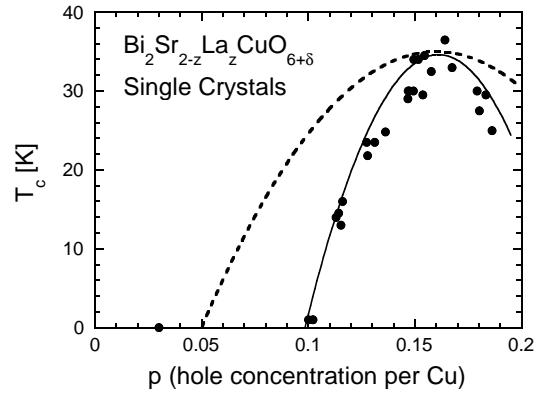


FIG. 5. Actual T_c (solid circles) and the fictitious T_c^0 (dashed line) plotted vs p for the BSLCO crystals. The p value is calculated from z by using $p = 0.21 - 0.13z$ [13]. The solid line is a guide to the eyes.

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